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Stability of Poly(amide acid) Solutions

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Stability of Poly(amide acid) Solutions

Objective

The objective of this work was to determine the stability of poly(amide acid) solutions stored at room temperature. The findings will impact resin handling procedures which may significantly affect processing conditions and properties of the polyimide.

Approach

The approach used to track solution stability of candidate poly(amide acid) (PAA) solutions is shown in Figure 1.

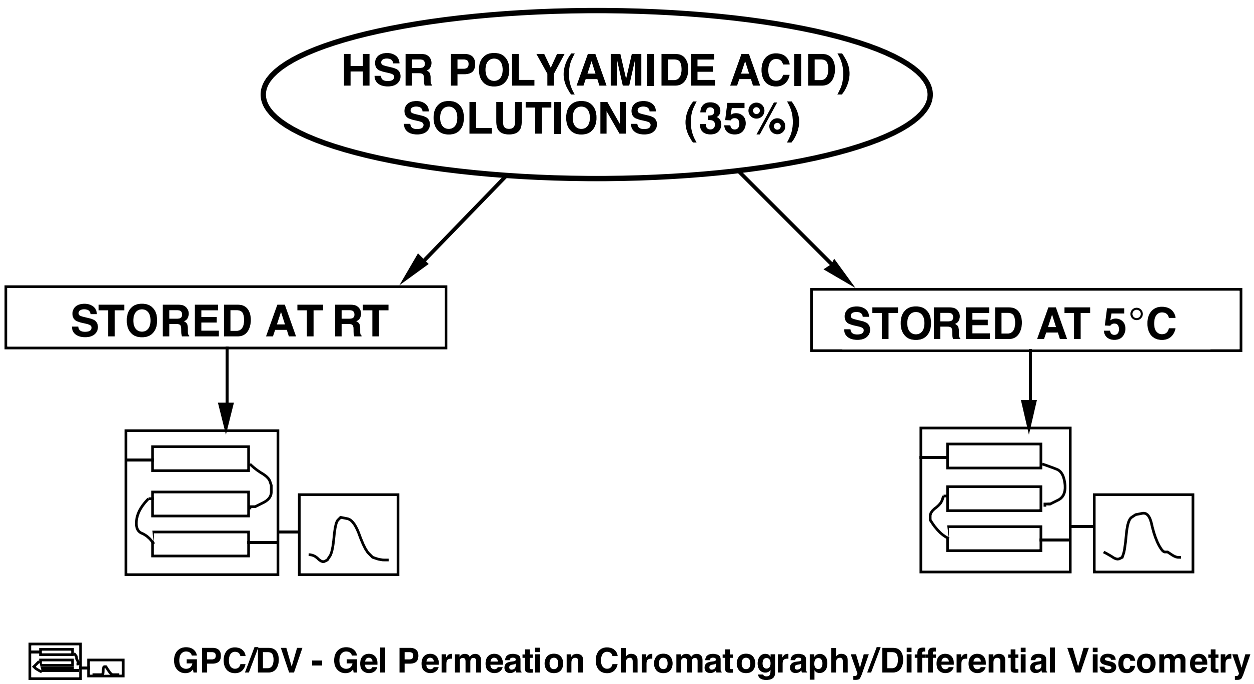


Figure 1: Schematic of approach used to investigate poly(amide acid) solution stability.

Poly(amide acid) solutions (~35% solids) in N-methyl pyrrolidinone (NMP) were stored in two vials, one at room temperature, and the other at 5°C (usual storage condition for poly(amide acid) solutions). The solutions were periodically sampled and analyzed using gel permeation chromatography/differential viscometry (GPC/DV) to obtain molecular weights, molecular weight distributions and intrinsic viscosities. Aging was carried out to several months.

Experimental

Four poly(amide acid)s as shown in Table 1 were studied.

TABLE 1
HSR Candidate Poly(amide acid) Solutions Used in Aging Study

SAMPLE	DESCRIPTION
PETI-5 (1,2)	Phenyl ethynyl terminated poly(amide acid)
PTPEAA-1 (3)	Pendent terminal phenyl ethynyl poly(amide acid)
PPEAA-1 (4)	Pendent phenyl ethynyl poly(amide acid)
80/20 PETI-5/additive (5)	PETI-5 blended with 20% viscosity lowering additive

The solvent used for chromatography was filtered, vacuum distilled NMP treated with 0.02M phosphorus pentoxide (NMP/0.02M P_2O_5). Solutions injected had concentrations of 3 mg/ml. The poly(amide acid) aged at 5°C was allowed to warm to room temperature in a dessicator for approximately an hour, before a small aliquot was removed for dilution. After this brief period at room temperature, the vial was returned to the refrigerator at 5°C.

The dilute solutions were prepared within 15 minutes of injection into the chromatograph. They were filtered through a teflon 0.2 µm filter prior to the run. Chromatography was performed on a three column bank consisting of a linear Waters Styragel HT 6E column, which covers a molecular weight range from 10^3 to 10^7 g/mol, in series with a Styragel HT 3 column, which covers the range from 5 x 10^2 to 3 x 10^4 g/mol and a Styragel HT 2 column, which covers the range from 10^2 to 10^4 g/mol. The Waters 150C Gel Permeation Chromatograph was equipped with a model 150R differential viscosity detector and a differential refractive index detector. Universal calibration curves were generated weekly using narrow molecular weight distribution polystyrene standards having molecular weights ranging from 500 to 2890000 g/mole.

Aged samples were analyzed daily for the first week, and twice weekly for several weeks thereafter. Sampling frequency tapered to once a week after a few months and finally to every other week.

Results and Discussion

The changes from initial values of molecular weights and intrinsic viscosities of the solutions are shown in Table 2. Data shown are for the first day and last day of data collection for each sample.

TABLE 2
Summary of Changes in Dilute Solution Properties of PAA Solutions

Day	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	[η] (dL/g)
PETI-5				
1	7914	13865	24260	0.258
263 (RT)	6898 (-12.8%)	11935 (-13.9%)	20325 (-16.2%)	0.230 (-10.9%)
263 (5°C)	7586 (-4.1%)	12975 (-6.4%)	21875 (-9.8%)	0.258
PTPEAA-1				
1	5952	14300	35200	0.255
220 (RT)	4460 (-25.1%)	10072 (-29.6%)	26600 (-24.4%)	0.222 (-12.9%)
220 (5°C)	5134 (-13.7%)	12170 (-14.9%)	29260 (-16.9%)	0.252 (-1.2%)
PPEAA-1				
1	5761	15950	40680	0.258
177 (RT)	4340 (-24.7%)	9988 (-37.4%)	24450 (-39.9%)	0.211 (-18.2%)
177 (5°C)	5278 (-8.4%)	12695 (-20.4%)	28373 (-30.3%)	0.251 (-2.7%)
80/20 PETI-5/Additive				
1	5377	13510	32615	0.275
164 (RT)	3260 (-39.4%)	4789 (-64.6%)	8234 (-74.8%)	0.194 (-29.5%)
164 (5°C)	4584 (-14.7%)	9456 (-30.0%)	19835 (-39.2%)	0.260 (-5.5%)

Percentages shown in parentheses quantify the decrease from the initial value of that parameter. An examination of the changes in molecular weights of room temperature aged samples shows that the most stable solution was PETI-5, which had the least change in molecular weights from initial values. The least stable system was the blend of 80/20 PETI-5/additive, where the higher moments of the molecular weight distribution were significantly lower with prolonged room temperature aging. Changes were usually largest for M_z, suggesting that lowering of molecular weights was due to loss of the longer chain species in the molecular weight distribution.

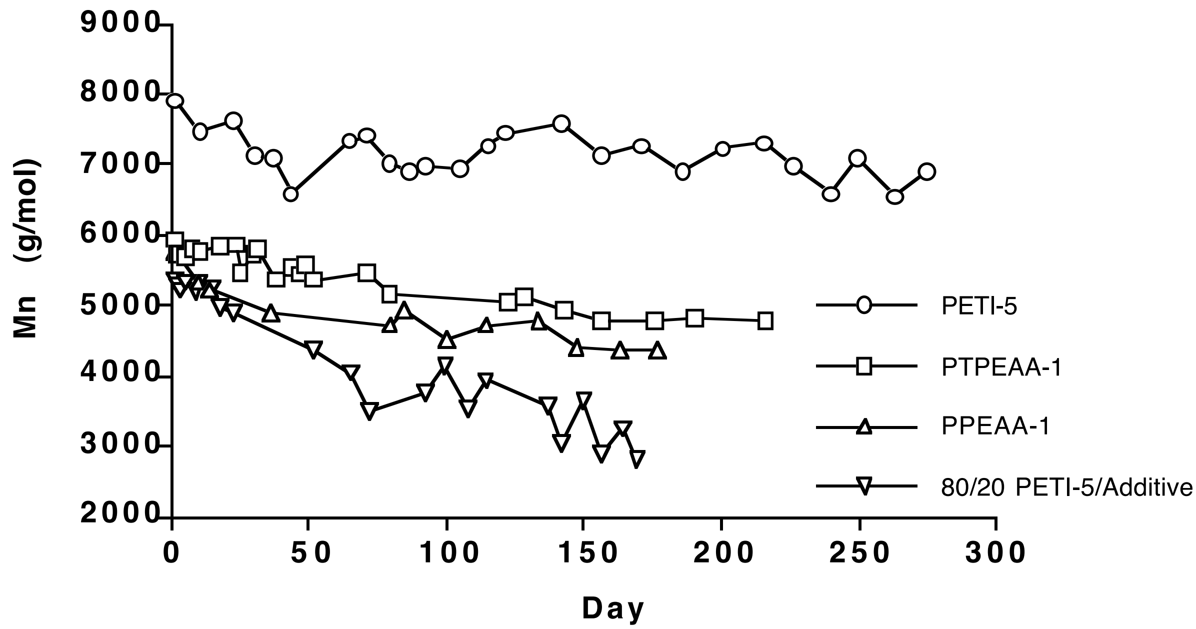
Although the samples stored at 5°C were meant to be controls and not expected to undergo aging, significant decreases in molecular weights were noted for three of the four systems studied. This suggests that the periodic warming of the solutions to room temperature for sample preparation purposes was enough to cause aging. For confirmation, a sample of PETI-5 received in September, 1995 and continuously stored at 5°C until May, 1996 was analyzed to determine if the molecular weights had changed during storage. Shown in Table 3 are the solution properties obtained for the sample when it was analyzed soon after receipt in September, 1995 and then again in July, 1996. No significant change was noted; therefore, 35% solutions are stable when stored continuously at 5°C.

TABLE 3
Comparison of Solution Properties for PETI-5 Lot 057-037

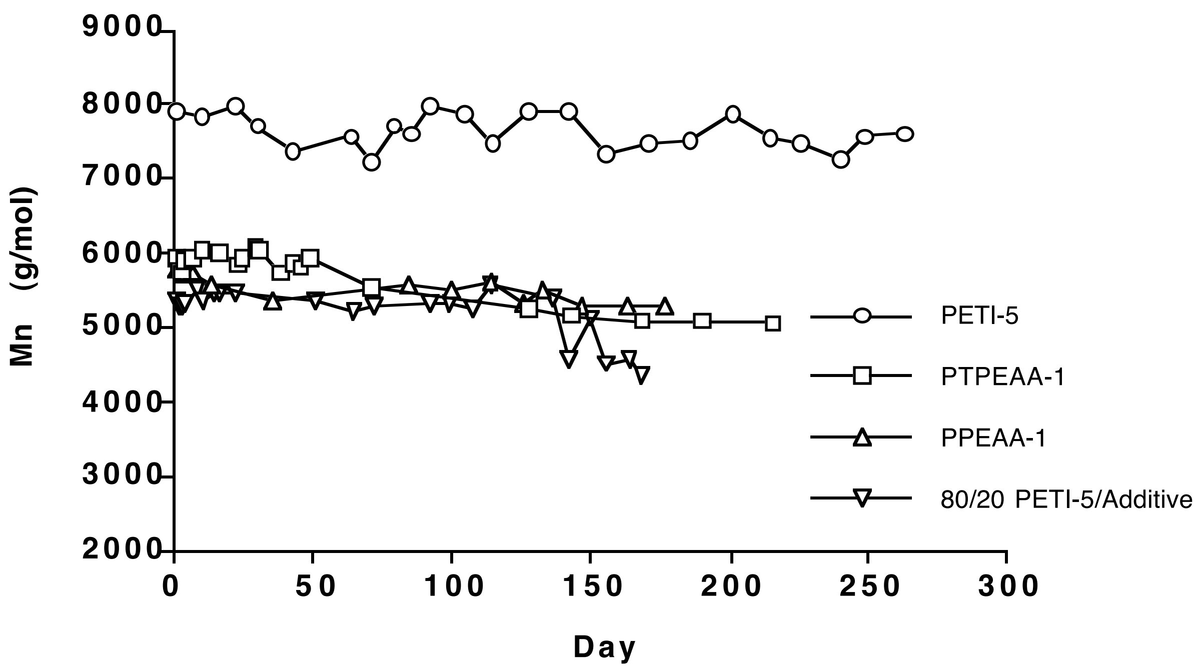
Date Characterized	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	$[\eta]$ (dL/g)
September, 1995	6864	16410	36970	0.283
May, 1996	6777	16910	38240	0.284

Although intrinsic viscosity ($[\eta]$) is often used to give an indication of the molecular weight of a sample due to its ease of measurement, data in Table 2 shows that $[\eta]$ is not sensitive enough to track the changes that the solution undergoes during aging. For instance, in the case of PTPEAA-1, a 1.2% decrease in $[\eta]$ may not seem important, but this translated to a 15% decrease in M_w which may be significant in determining processing conditions for the resin.

Figures 2-5 show the rate at which changes in the various molecular weight averages and intrinsic viscosity occurred for all the systems investigated.

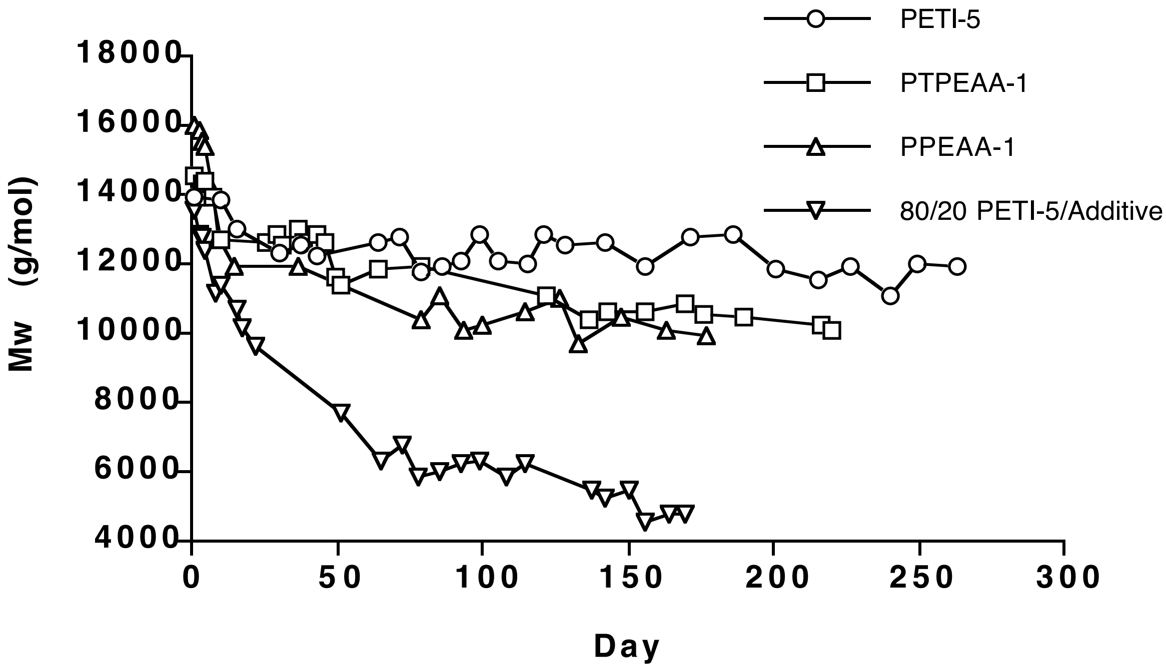


a) Room Temperature

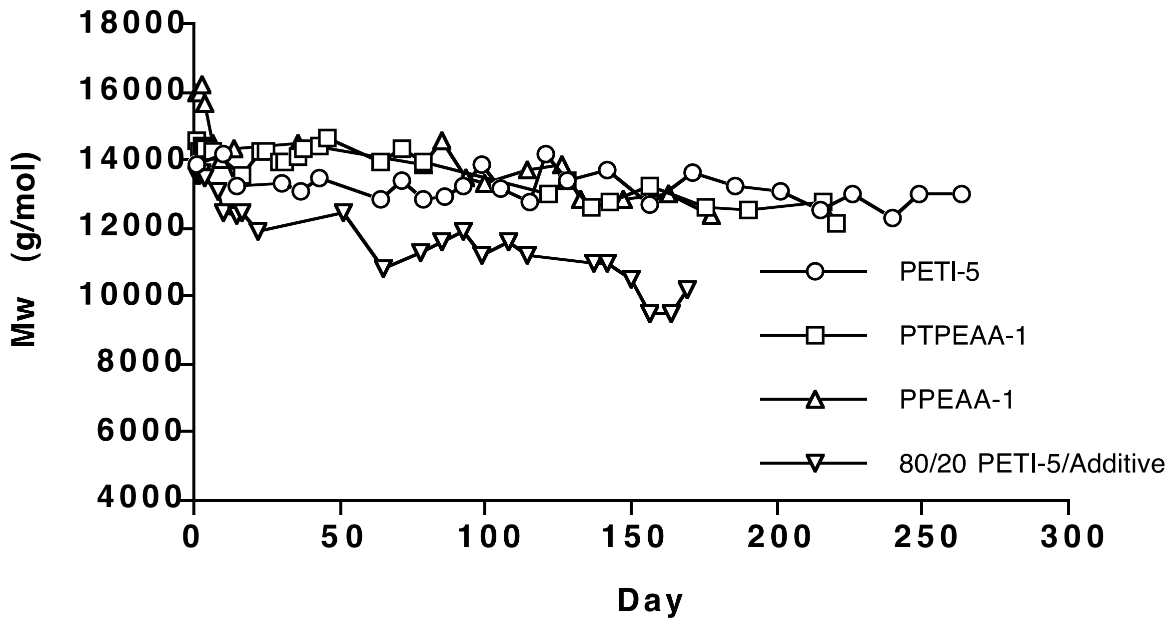


b) Refrigerated at 5°C

Figure 2: Changes in M_n for poly(amide acid) solutions stored at room temperature and at 5°C.

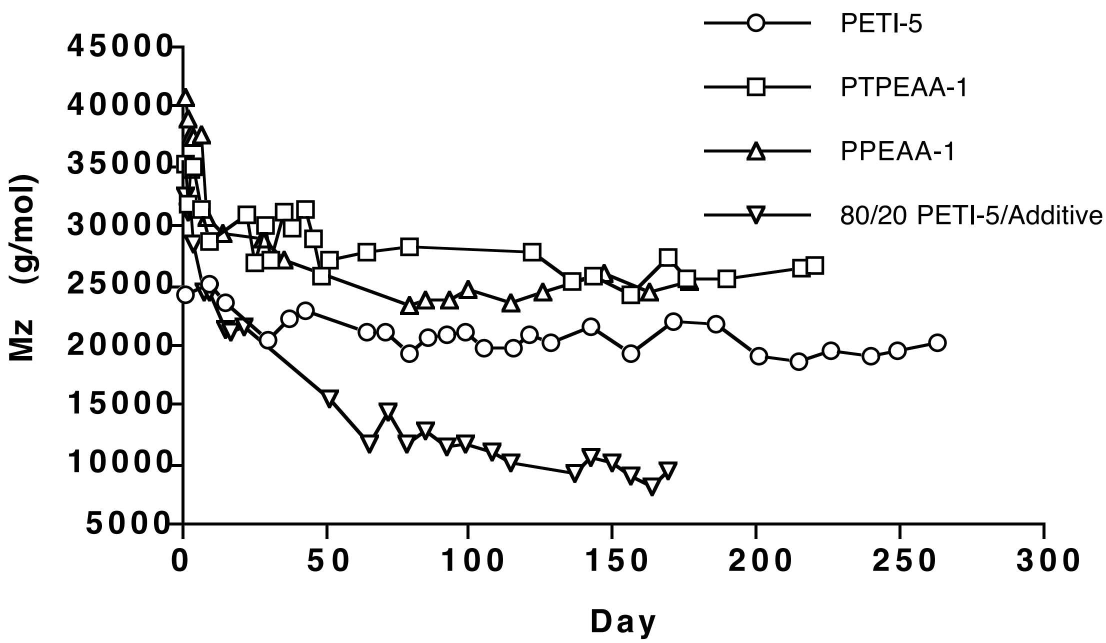


a) Room temperature

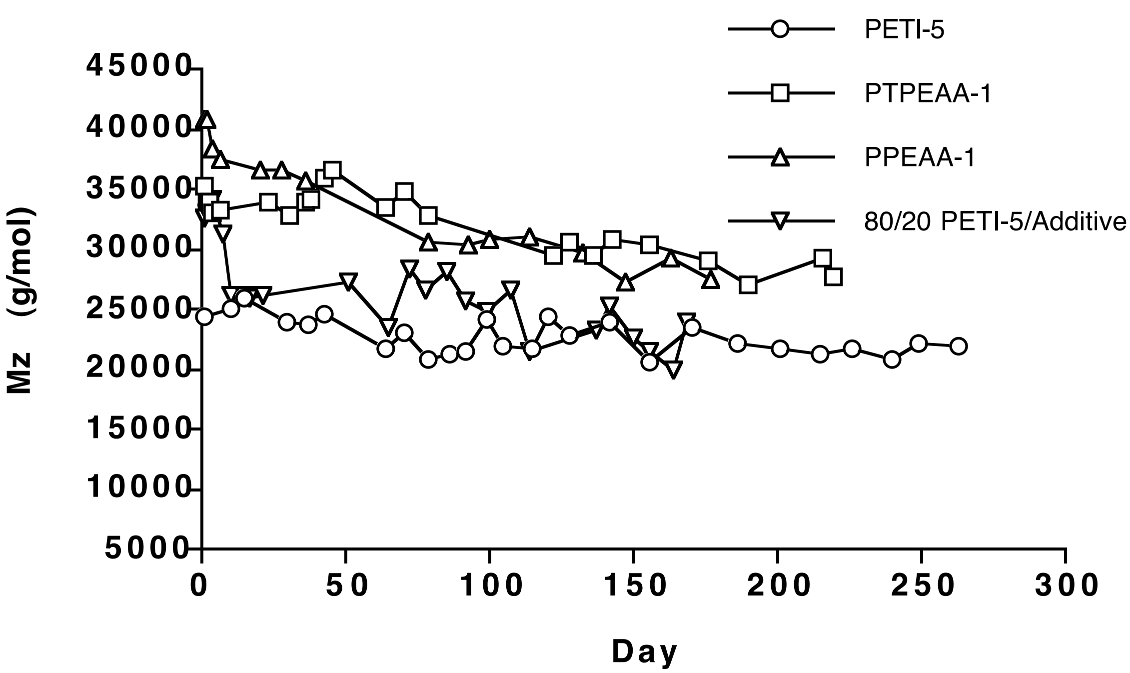


b) Refrigerated at 5°C

Figure 3: Changes in M_w for poly(amide acid)s stored at room temperature and at 5°C.

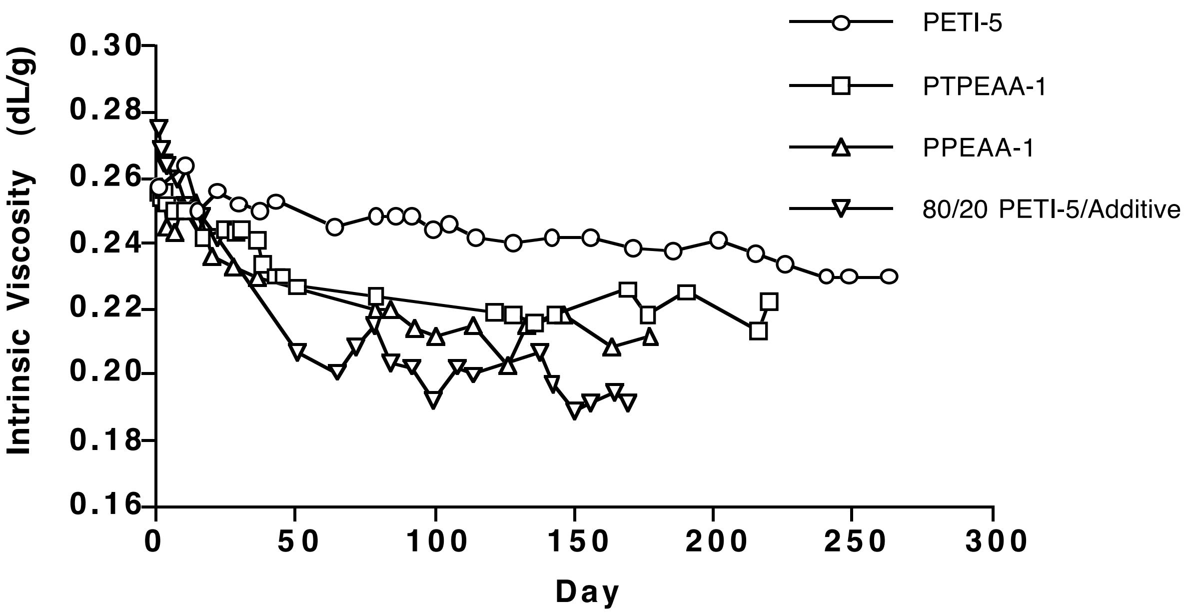


a) Stored at room temperature

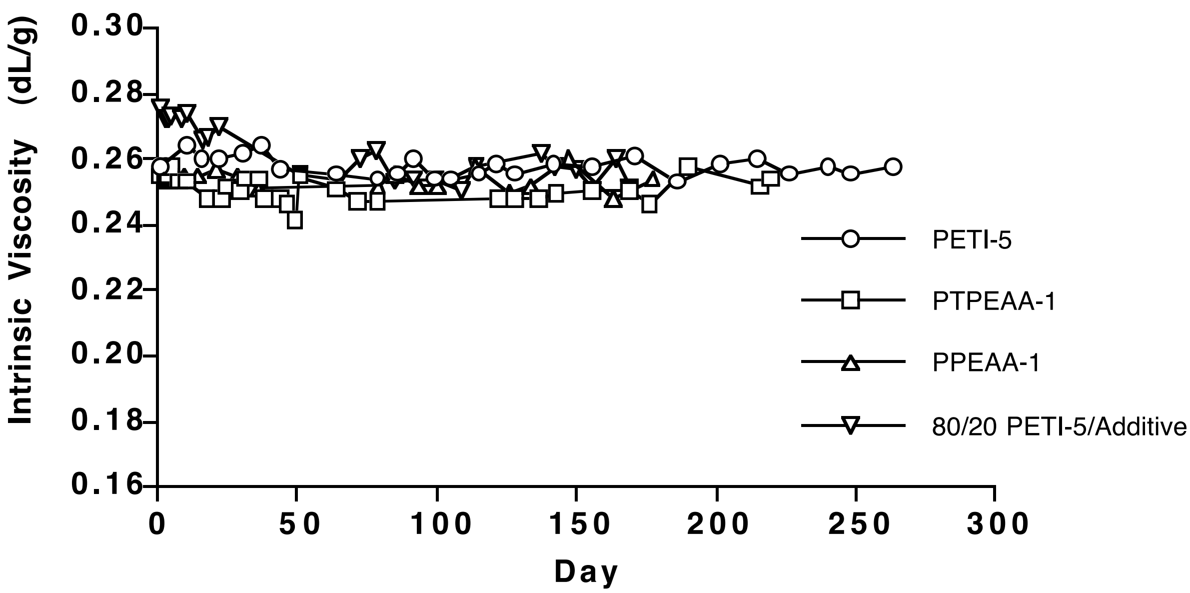


b) Refrigerated at 5°C

Figure 4: Changes in M_Z of poly(amide acid)s aged at room temperature and at 5°C.



a) Stored at room temperature



b) Refrigerated at 5°C

Figure 5: Changes in intrinsic viscosity of poly(amide acid)s stored at room temperature and at 5°C.

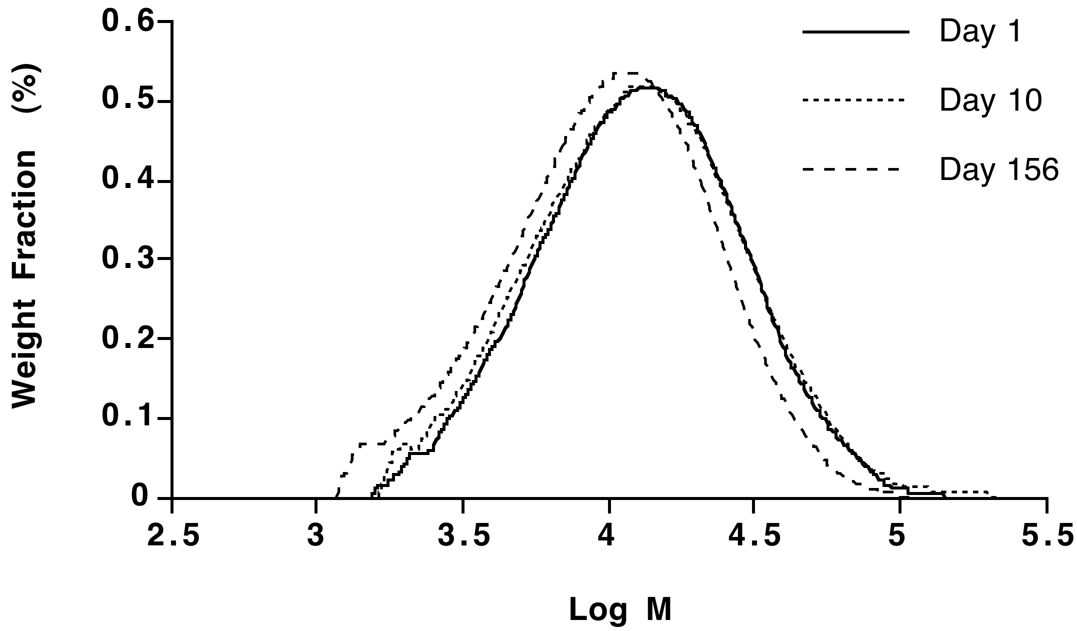
Figure 2 shows that for all systems, except for the 80/20 PETI-5/additive blend, M_n decreased at a faster rate within the first 50 days before levelling off at longer aging times. There was very little change in M_n for the samples stored at 5°C. For the blend, the rate of M_n changes did not slow down until about the 75th day.

Figure 3 is a summary of the changes that occurred in the second moment of the molecular weight distribution. There was a significant drop in M_w for three systems during the first 25 days, before the molecular weights decreased very slowly or remained fairly stable afterwards. The decrease in M_w for 80/20 PETI-5/additive blend did not slow down until about the 75th day, after which there was some levelling of the values. In all cases, changes in solutions stored at 5°C were less than those observed at room temperature.

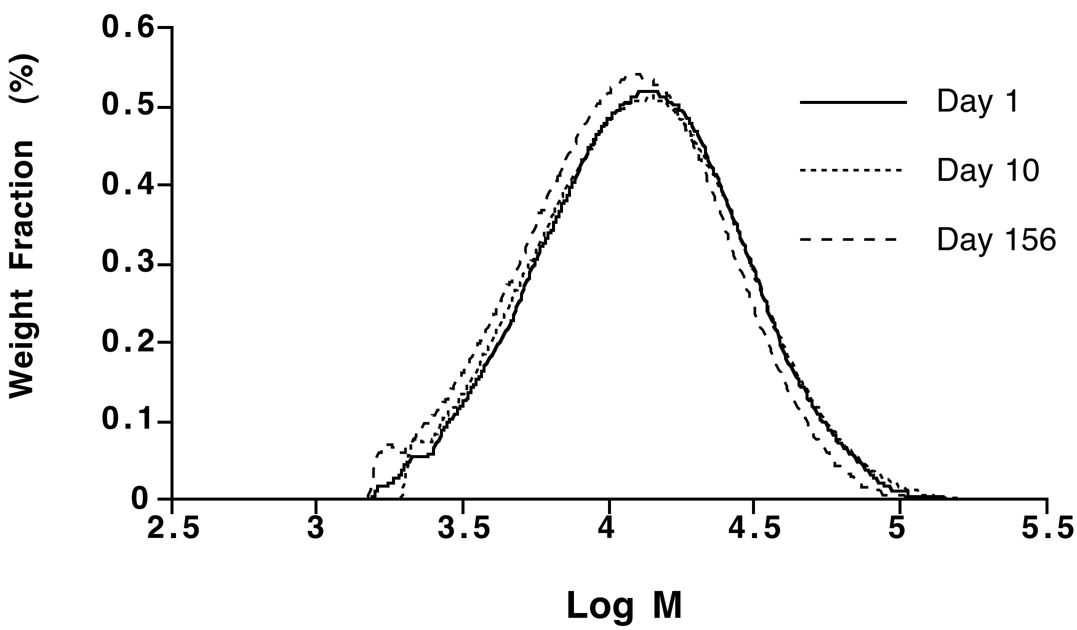
Figure 4 summarizes changes observed in M_z upon aging of the solutions. Of the three molecular weight averages measured, initial decreases in molecular weights were most noticeable in M_z, the parameter most affected by high molecular weight species. Since changes were more significant at the higher moments of the distribution which are greatly influenced by higher molecular weight species, processing may be affected by the molecular weight of the solution at the time it is to be processed.

Figure 5 shows changes in intrinsic viscosity for all the solutions. Although there were larger decreases from initial intrinsic viscosity values with room temperature aging, the changes do not reflect the large drops observed in molecular weight values.

Changes in the distribution of molecular weights as the various molecular weight averages decreased are shown in Figures 6-9 for the poly(amide acid)s. Data shown are for molecular weight distributions obtained for solutions aged at room temperature (designated as Figure _a) and at 5°C (designated as Figure _b). Overlays of three distributions are shown in each figure, with the first one being that obtained on the first day of aging, a second one for an intermediate distribution measured after approximately 1 week of aging, and finally a distribution obtained after several months of aging. The aging time for final distribution was chosen to be a common day, where possible, so that fair comparison of the solution stabilities can be made.

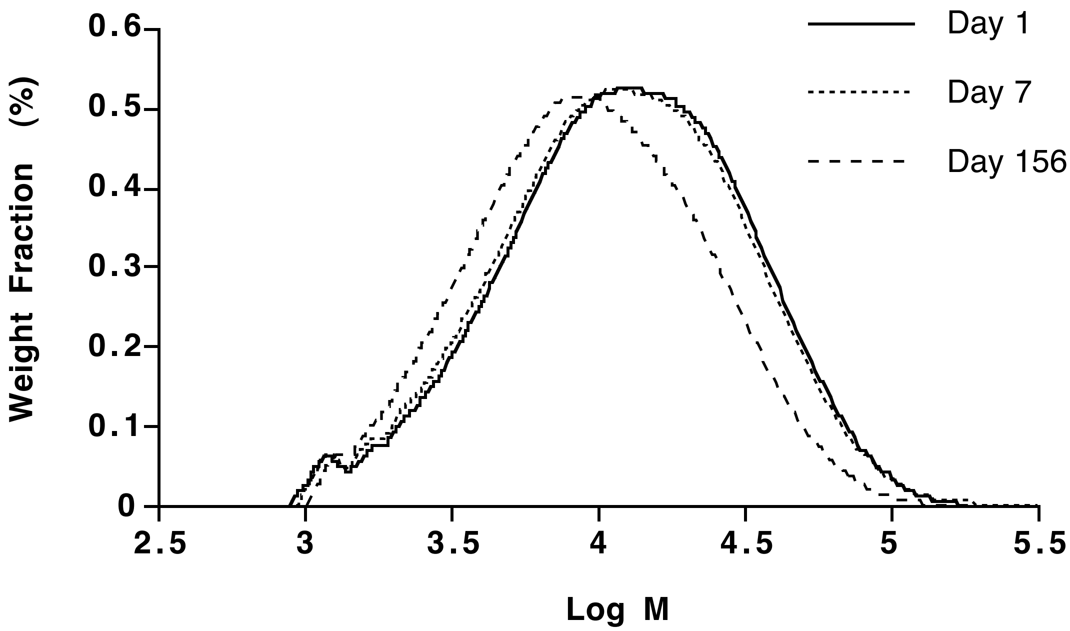


a) Stored at room temperature

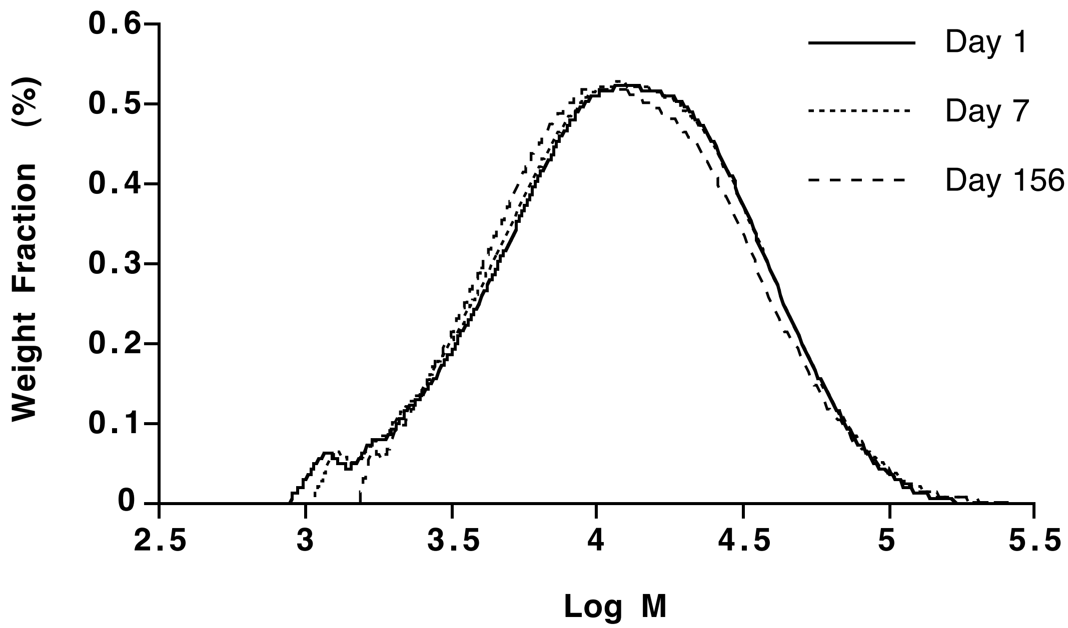


b) Refrigerated at 5°C

Figure 6: Changes in molecular weight distributions of PETI-5 PAA solutions aged at room temperature and at 5°C.

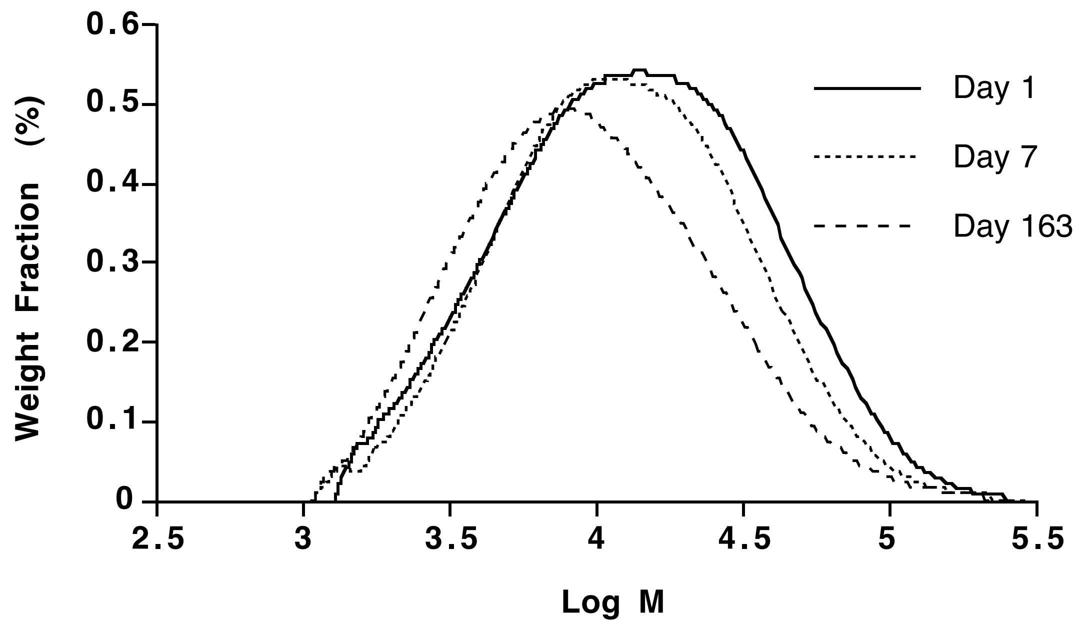


a) Stored at room temperature

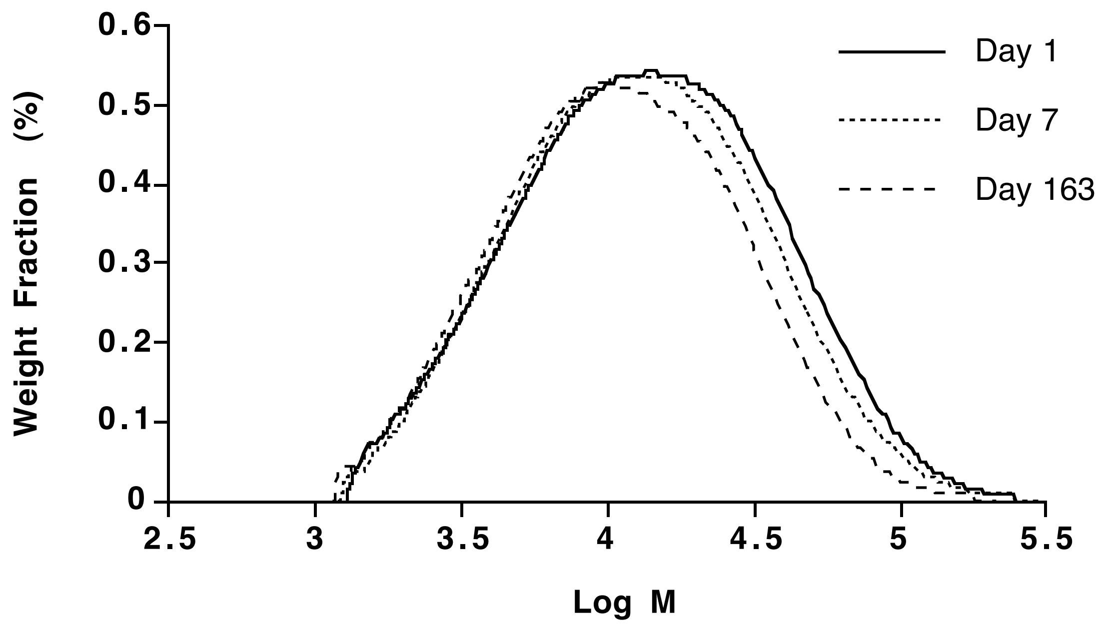


b) Refrigerated at 5°C

Figure 7: Changes in molecular weight distributions of PTPEAA-1 solutions aged at room temperature and at 5°C.

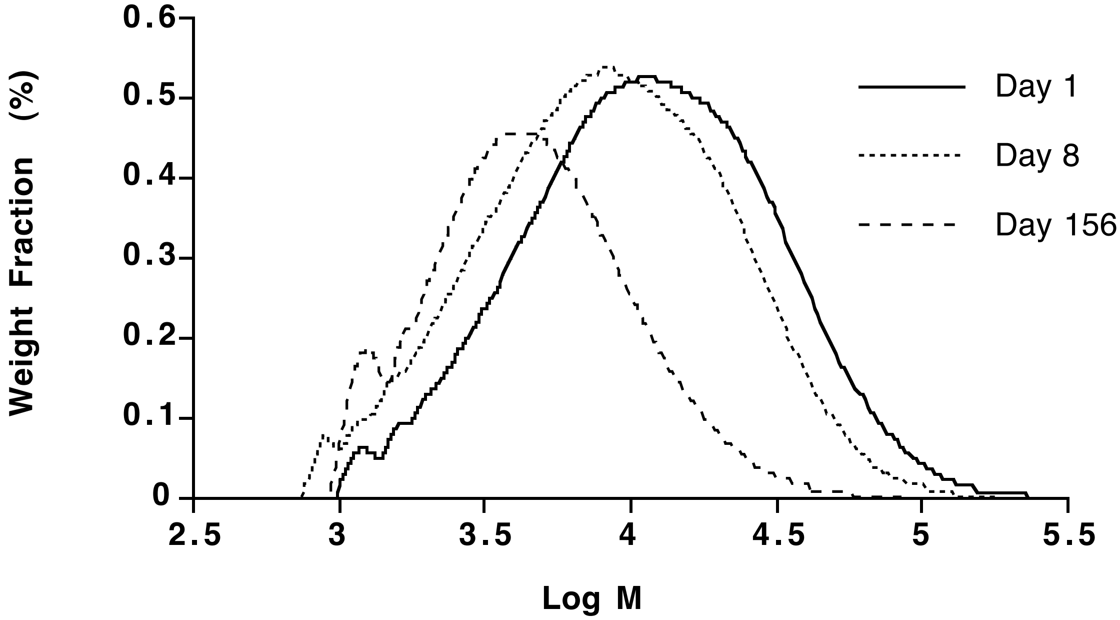


a) Stored at room temperature.

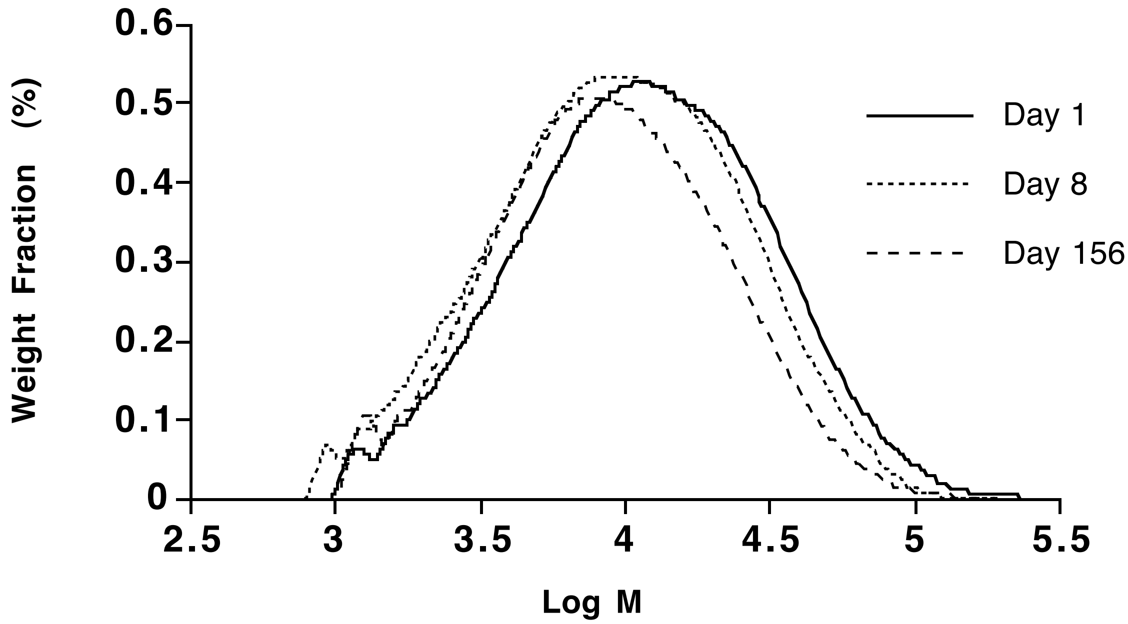


b) Refrigerated at 5°C

Figure 8: Changes in molecular weight distributions of PPEAA-1 solutions aged at room temperature and at 5°C.



a) Stored at room temperature



b) Refrigerated at 5°C

Figure 9: Changes in molecular weight distributions of 80/20 PETI-5/additive aged at room temperature and 5°C.

Data shown in Figures 6-9 confirm that PETI-5 was the most stable, with almost no change occurring in the molecular weight distribution after 10 days of aging at room temperature. PTPEAA-1 showed only a slight shift to lower molecular weights after 7 days at room temperature. Significant shifts to lower molecular weights are observed in PPEAA-1 and 80/20 PETI-5/additive as seen in Figures 8 and 9.

Shifts to lower molecular weights after prolonged storage at room temperature may be due to equilibration of polymer chains in solution. However, after about 160 days, the shape of the molecular weight distribution for 80/20 PETI-5/additive was different from its original shape, suggesting that significant changes in the solution may be due to degradation. This is likely due to the presence of the low molecular weight additive.

Conclusions

This investigation into the behavior of concentrated poly(amide acid) solutions at room temperature revealed that solution stability is affected by the backbone structure of the polymer. Specifically, stability decreased in the order PETI-5 > PTPEAA-1 > PPEAA-1 > PETI-5/additive. The addition of a low molecular weight additive to PETI-5 resulted in large decreases in all the molecular weight averages. This was not surprising since poly(amide acid)s are known to undergo chain equilibration upon aging.

The results indicate that care should be taken in handling the poly(amide acid) solutions prior to and during processing. Storage at 5°C is appropriate and solutions should not be allowed to be exposed unnecessarily at room temperature for prolonged periods of time. It was noted that large decreases in molecular weights occurred mostly within the first two to three weeks of the aging experiment. Based on previous work done in-house, it is known that changes in molecular weights like those observed at long aging times affect processing parameters for the solutions.

Finally, although intrinsic viscosity is an easy parameter to measure, it was not sensitive enough to reflect large changes occurring in molecular weights; therefore, $[\eta]$ is not sufficient to determine proper processing conditions for concentrated poly(amide acid) solutions. It is important to obtain molecular weight distributions for this purpose.

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Aging characteristics of four poly(amide acid) solutions were followed using gel permeation chromatography. NASA LaRC™PETI-5 was found to be the most stable over a period of about 270 days.

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